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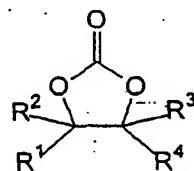
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(54) Non-aqueous electrolytic solution for capacitor and capacitor containing non-aqueous electrolytic solution

(57) A non-aqueous electrolytic solution for capacitors comprising a non-aqueous solvent containing at least one cyclic carbonic ester selected from compounds (1), (2) and (3) and an electrolyte; wherein

(1) is a compound of Formula (I):



(I)

wherein R¹ to R⁴, which may be the same or different, are each hydrogen, optionally substituted alkyl, an optionally substituted unsaturated hydrocarbon group, optionally substituted aryl or a group represented by -CH₂-O-A in which A is R⁵, CO-R⁵ or CO-O-R⁵ and R⁵ is alkyl or an unsaturated hydrocarbon group; said compound being such that:

(i) at least one of R¹ to R⁴ is -CH₂-O-A, with the remaining groups selected from hydrogen, optionally substituted alkyl and an optionally substituted unsaturated hydrocarbon group; or

(ii) at least one of R¹ to R⁴ is an optionally substituted unsaturated hydrocarbon group, with the remaining

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Description**TECHNICAL FIELD**

5 [0001] The present invention relates to a non-aqueous electrolytic solution for capacitors which contains primarily cyclic carbonic ester, specifically a non-aqueous electrolytic solution for electric double layer capacitors, more specifically a capacitor showing high energy density and excellent with-stand voltage and charging/ discharging cycle properties, and especially a non-aqueous electrolytic solution that can provide electric double layer capacitors.

TECHNICAL BACKGROUND

10 [0002] Up to the present, capacitors, particularly electric double layer capacitors having a capacity intermediate between that of a battery and that of a capacitor, as a backup power supply for IC's and memories and a supplement or alternative to secondary batteries, have been used widely as a low-power direct-current power supply. In recent 15 years, however, there have been new portable electronic devices coming into being one after another, such as VTR with a built-in camera, cellular phones and laptop computers. Amid this trend, there has been a growing demand that those electric double layer capacitors used as a backup power supply and a supplement or alternative to secondary batteries should have higher energy density.

20 [0003] These electric double layer capacitors, unlike batteries, do not convert a chemical change into electric energy. They utilize a large capacity of the electric double layer that occur between the electrodes and the electrolytic solution to put in and out an electric charge in the same manner as the charge and discharge of batteries. Such electric double layer capacitors are normally so constructed that they use a non-corrosive electrolytic solution that does not corrode the capacitor container or the collector made of aluminum, copper or the like and two electrodes formed from a material having a large surface area such as activated carbon and a binder such as fluororesins are so arranged that they face 25 each other via a porous separator made of polyethylene or polypropylene.

30 [0004] As the electrolytic solution for such electric double layer capacitors, aqueous-solution-based electrolytic solution and organic-solvent-based electrolytic solution (non-aqueous electrolytic solution) are used. However, aqueous-solution-based electrolytic solution showing low potential window of electrochemical stability (approx. 1.2 V) are difficult to provide high-energy-density electric double layer capacitors.

35 [0005] By contrast, compared with aqueous-solution-based electrolytic solution, organic-solvent-based electrolytic solution (non-aqueous electrolytic solution) show high potential window of electrochemical stability and therefore make the formation of high-energy-density capacitors possible. Because of this, the electric double layer capacitors using non-aqueous electrolytic solution are beginning to come into use rapidly as a backup power supply for electronic equipment for non-military use.

40 [0006] As such non-aqueous electrolytic solution, a mixture of a non-aqueous solvent such as cyclic carbonic ester having exhibiting a high dielectric constant and an electrolyte such as tetraethylammonium tetrafluoroborate, for example, is used.

45 [0007] However, such electrolytic solution as mentioned above has had the problem of the inner electrical resistance of the capacitor going up due to its low electric conductivity, making it difficult to obtain high-output capacitors. Furthermore, when future capacitors have high energy density, the aforementioned electrolytic solution might be insufficient in potential window of electrochemical stability. Because of this, it has been hoped that a non-aqueous electrolyte having better charging/discharging cycle properties will come into existence.

SUMMARY

50 [0008] The inventors of the present invention sought a solution to the problems of the conventional technology as described above. The present invention is intended to provide non-aqueous electrolytic solutions which release a little gas, have excellent potential window of electrochemical stability and enable capacitors to show excellent charging/ discharging cycle properties and safety performance, and capacitors containing such non-aqueous electrolytic solutions.

55 [0009] The non-aqueous electrolytic solution for capacitors of the present invention comprises an electrolytic solution containing at least one cyclic carbonic ester selected from compounds of the following (1), (2) and (3) and an electrolyte:

(1) A compound which is represented by Formula (I):

the metal case as a part integral with the sealing part.

DETAILED DESCRIPTION

5 [0015] Given below is a specific description of the non-aqueous electrolytic solutions and capacitors of the present invention.

NON-AQUEOUS ELECTROLYTIC SOLUTION FOR CAPACITORS

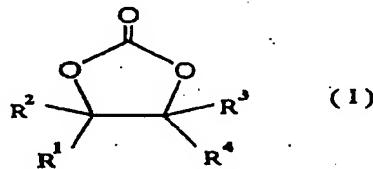
10 [0016] The non-electrolytic solution of the present invention comprises the non-aqueous solvent containing cyclic carbonic ester and an electrolyte.

Cyclic carbonic ester:

[0017] Given below is a specific description of cyclic carbonic ester.

[0018] First, an explanation is given of the compound (1) which is represented by Formula (I):

15



20

(wherein R¹ to R⁴, which may be the same or different, are hydrogen, the alkyl group, the unsaturated hydrocarbon group or the aryl group or a group represented by -CH₂-O-A, wherein A stands for R⁵, CO-R⁵ or CO-O-R⁶ [wherein R⁶ is the alkyl group or the unsaturated hydrocarbon group]); said compound being such that:

25 (i) In Formula I, at least one of R¹ to R⁴ is the aforementioned group represented by -CH₂-O-A, with the remaining groups selected from among hydrogen, the alkyl group and the unsaturated hydrocarbon group.

30 (ii) In Formula I, at least one of R¹ to R⁴ is the unsaturated hydrocarbon group, with the remaining groups selected from among hydrogen, the alkyl group, the aryl group and the unsaturated hydrocarbon group.

(iii) In Formula I, R¹ to R⁴ are selected from among the alkyl group and the aryl group.

35 [0019] In Formula (I), as examples of the alkyl group, a straight-chain or branched alkyl group having 1 to 20 carbon atoms, preferably an alkyl group having 1 to 6 carbon atoms, more preferably an alkyl group having 1 to 4 carbon atoms can be cited. Examples include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, neopentyl and n-hexyl. Out of them, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl are most preferable. As examples of the unsaturated hydrocarbon group, a straight-chain or branched unsaturated hydrocarbon group having 2 to 20 carbon atoms, preferably an unsaturated hydrocarbon group having 2 to 6 carbon atoms, more preferably an unsaturated hydrocarbon group having 2 to 4 carbon atoms can be cited. Specific examples include straight-chain or branched alkenyl groups such as vinyl, allyl and isopropenyl and straight-chain or branched alkinyl groups such as ethynyl and propargyl. As examples of the aryl group, aryl groups having 6 to 30 carbon atoms, preferably 6 to 12 carbon atoms, such as phenyl, benzyl, naphthyl, biphenyl, terphenyl, phenanthryl and anthracenyl can be cited.

40 [0020] The aforementioned alkyl group, unsaturated hydrocarbon group and aryl group may have a substituent group. Such substituent group may be the aforementioned alkyl group, aryl group and unsaturated hydrocarbon group, for example. In other words, the alkyl group, unsaturated hydrocarbon group and aryl group may be an alkyl-substituted unsaturated hydrocarbon group, alkyl-substituted aryl group, aryl-substituted alkyl group and aryl-substituted unsaturated hydrocarbon group, for example. As another preferable example of such substituent group, an oxygen-containing group can be cited.

45 [0021] Examples of such oxygen-containing group include the alkoxy group, aryloxy group, alkanoyloxy group, alkenoyloxy group, ester group, acyl group, acyloxy group, carboxyl group, carbonate group, hydroxy group, peroxy group and carboxylic acid anhydride group. Out of these, the alkoxy group, aryloxy group, acyl group, particularly alkanoyl group and alkenoyl group, acyloxy group, particularly alkanoyloxy group and alkenoyloxy group can be cited as preferable examples. As examples of the alkoxy group, preferably an alkoxy group having 1 to 30 carbon atoms, more preferably an alkoxy group having 1 to 6 carbon atoms, can be cited. Specific examples include methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, isobutoxy and tert-butoxy. As examples of the aryloxy group, an aryloxy group having 6 to 30 carbon atoms, preferably an aryloxy group having 6 to 12 carbon atoms, can be cited. Specific examples include phenoxy group, 2,6-dimethylphenoxy group and 2,4,6-trimethylphenoxy group.

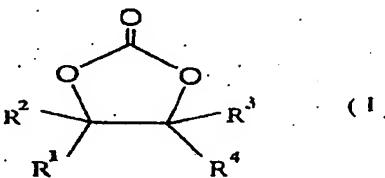
and particularly the vinyl group and the isopropenyl group are used preferably. Furthermore, at least one of R¹ to R⁴ of the cyclic carbonic ester(B) represented by the aforementioned Formula (I) is -CH₂-O-CO-X (wherein X is hydrogen atom, an alkyl group having 1 to 6 carbon atoms or an unsaturated hydrocarbon group having 2 to 6 carbon atoms) and the remaining groups, which may be the same or different, are preferably H, -CH₃, -C₂H₅ or -CH=CH₂.

[0023] Examples of such cyclic carbonic ester(B) include

10 4-acetoxymethyl-1,3-dioxolane-2-one,
 4-propionyloxymethyl-5-vinyl-1,3-dioxolane-2-one,
 4-acryloyloxymethyl-1,3-dioxolane-2-one,
 4-acryloyoxymethyl-5-methyl-1,3-dioxolane-2-one,
 4-acryloyoxymethyl-4-vinyl-1,3-dioxolane-2-one,
 4-methacryloyoxymethyl-1,3-dioxolane-2-one,
 15 4-methacryloyoxymethyl-5-vinyl-1,3-dioxolane-2-one,
 4-methacryloyoxymethyl-4-vinyl-1,3-dioxolane-2-one,
 4-methacryloyoxymethyl-4,5-dimethyl-1,3-dioxolane-2-one,
 4-(3'-butenoyloxymethyl)-1,3-dioxolane-2-one,
 4-(3'-butenoyloxymethyl)-5-allyl-1,3-dioxolane-2-one,
 20 4-(3'-butenoyloxymethyl)-5-methoxymethyl-1,3-dioxolane-2-one, 4-(2'-butenoyloxymethyl)-5-allyloxymethyl-1,3-dioxolane-2-one, 4-(2'-butenoyloxymethyl)-4-ethyl-5-methyl-1,3-dioxolane-2-one and
 4-(3'-butynoyloxymethyl)-1,3-dioxolane-2-one.

25 Out of these, 4-acryloyloxymethyl-1,3-dioxolane-2-one, and 4-methacryloyoxymethyl-5-vinyl-1,3-dioxolane-2-one are used especially preferably.

(C) The cyclic carbonic ester which is a cyclic carbonic ester which is represented by the following (I):



40 wherein at least one of R¹ to R⁴ is a group represented by -CH₂-O-COO-X (wherein X is hydrogen atom, an alkyl group having 1 to 6 carbon atoms or an unsaturated hydrocarbon group having 2 to 6 carbon atoms) and the remaining groups, which may be the same or different, are any of hydrogen atom, an alkyl group having 1 to 6 carbon atoms, an unsaturated hydrocarbon group having 2 to 6 carbon atoms, a hydrocarbon group having 1 to 6 carbon atoms and containing the alkoxy group, alkanoyloxy group or alkenoyloxy group and an unsaturated hydrocarbon group having 2 to 6 carbon atoms and containing the alkoxy group.

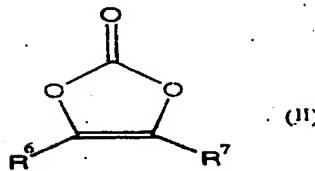
45 In the aforementioned Formula (I), X is preferably an unsaturated hydrocarbon group having 2 to 6 carbon atoms, and particularly the allyl group and the 1-propenyl group are used preferably.

Furthermore, the R¹ to R⁴ of the cyclic carbonic ester represented by the aforementioned Formula (I) with the exception of -CH₂-O-COO-X are preferably H, -CH₃, -C₂H₅ or -CH=CH₂.

[0024] Specific examples of such cyclic carbonic ester (C) include

50 4-methoxycarbonyloxymethyl-1,3-dioxolane-2-one,
 4-methoxycarbonyloxymethyl-5-vinyl-1,3-dioxolane-2-one,
 4-methoxycarbonyloxymethyl-5-allyloxymethyl-1,3-dioxolane-2-one, 4-ethoxycarbonyloxymethyl-1,3-dioxolane-2-one, 4-ethoxycarbonyloxymethyl-5-methoxymethyl-1,3-dioxolane-2-one,
 4-allyloxycarbonyloxymethyl-1,3-dioxolane-2-one,
 55 4-allyloxycarbonyloxymethyl-5-methyl-1,3-dioxolane-2-one, 4-allyloxycarbonyloxymethyl-4-vinyl-1,3-dioxolane-2-one, 4-allyloxycarbonyloxymethyl-5-allyl-1,3-dioxolane-2-one, 4-allyloxycarbonyloxymethyl-5-(1'-propenyl)-1,3-dioxolane-2-one,
 4-(1'-propenyl)-1,3-dioxolane-2-one,

5



(wherein R⁶ and R⁷, which may be the same or different, are the alkyl group or the unsaturated hydrocarbon group).

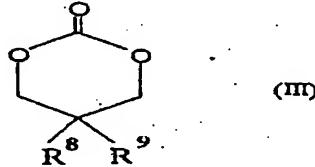
[0033] In the Formula, R⁶ and R⁷, which may be the same or different, are preferably an alkyl group having 1 to 4 carbon atoms or the unsaturated hydrocarbon group having 2 to 4 carbon atoms.

[0034] Examples of such cyclic carbonic ester(2) include vinylene carbonate, 4,5-dimethylvinylene carbonate and 4-ethylvinylene carbonate.

[0035] The preferable examples of cyclic carbonic ester(3) are vinylene carbonate, 4-methylvinylene carbonate and 4,5-dimethylvinylene carbonate whose R⁶ and R⁷ are hydrogen atom or the methyl group.

[0036] Below is given an explanation of the compound(3) represented by Formula (III).

20



25

wherein R⁸ and R⁹, which may be the same or different, are the alkyl group, the aryl group or the unsaturated hydrocarbon group.

[0037] Examples of such cyclic carbonic ester(3) include 5,5-dimethyl-1,3-dioxane-2-one, 5,5-diethyl-1,3-dioxane-2-one, 5,5-divinyl-1,3-dioxane-2-one, 5-vinyl-5-methyl-1,3-dioxane-2-one and 5-ethyl-5-methyl-1,3-dioxane-2-one.

30

[0038] The preferable examples of the cyclic carbonic ester(3) are 5,5-dimethyl-1,3-dioxane-2-one and 5,5-diethyl-1,3-dioxane-2-one whose R⁸ and R⁹ are CH₃ or C₂H₅.

35

[0039] Such cyclic carbonic ester represented in (1), (2) and (3) above shows excellent acid resistance, is not oxidized when allowed to stand in the atmosphere, and is chemically stable without reacting with water under normal storage conditions or reacting with highly reactive substances such as metal lithium. Furthermore, such cyclic carbonic ester has the properties of being physically safe, being not readily decomposed thermally and being flame-retardant and resistant to electrochemical oxidation or reduction.

40

[0040] Therefore, such cyclic carbonic ester can be used suitably for a solvent for the electrolytic solutions for use in capacitors, batteries and electrochemical reaction. Moreover, such cyclic carbonic ester can be used suitably in pharmaceuticals, agrochemicals, acrylic fiber processing agents, polymer compound solvents and organic intermediates. Non-aqueous solvent for electrolytic solution:

[0041] In the present invention, non-aqueous solvents containing the aforementioned cyclic carbonic ester are used as the solvent for electrolytic solution. Such solvent may be one or more solvents of the aforementioned cyclic carbonic ester or a mixed solvent with another solvent.

45

[0042] Examples of such another solvent include cyclic carbonic esters such as ethylene carbonate, propylene carbonate, butylene carbonate and vinylene carbonate; chain carbonic esters such as dimethyl carbonate, methylethyl carbonate, diethyl carbonate, methylpropyl carbonate and methylisopropyl carbonate; cyclic esters such as γ -butyrolactone, 3-methyl- γ -butyrolactone and 2-methyl- γ -butyrolactone; chain esters such as methyl formate, ethyl formate, methyl acetate, ethyl acetate, propyl acetate, methyl propionate, methyl butyrate and methyl valerate; cyclic ethers such as 1,4-dioxane, 1,3-dioxolane, tetrahydrofuran, 2-methyl tetrahydrofuran and 3-methyl-1,3-dioxolane; chain ethers such as 1,2-dimethoxyethane, 1,2-diethoxyethane, diethylether, dimethylether, methylethylether and dipropyl-ether; and sulfur-containing compounds such as sulfolane.

55

[0043] Further, as cyclic carbonic ester, the cyclic carbonic ester having the halogen atom-substituted alkyl group described in Japanese Laid-open Patent Publication HEI 9-63644 may be used in addition to the aforementioned cyclic carbonic esters given as examples. Examples of such cyclic carbonic ester include monofluoromethylene carbonate, difluoromethylene carbonate and trifluoromethyl-ethylene carbonate.

[0044] These solvents may be used singly or in combination with one or not less than two of them.

[0045] In the present invention, if the cyclic carbonic ester represented in (1), (2) and (3) above and another solvent are mixed, the cyclic carbonic ester represented in (1), (2) and (3) above is contained in such electrolyte solvent pref-

the same effect can also be achieved by using the electrolytic solution of the present invention in other electric double layer capacitors having a structure different from that of the wound-type electric double layer capacitor, such as the electric double layer capacitor of the coin type described in the Japanese Published Patent HEI 3-51284 Publication and the electric double layer capacitor of the laminated type described in the Japanese Laid-open Patent HEI 8-78291 Publication.

EXAMPLES

[0058] In the following examples are described several preferred embodiments to illustrate the present invention. However, it is to be understood that the present invention is not intended to be limited to the specific embodiments.

[0059] In this patent application, the evaluation of the potential window of electrochemical stability of the electrolytic solution and the charging/discharging test were conducted as described below.

[0060] The results are shown in Table 1.

15 Potential window of electrochemical stability:

[0061] The aforementioned electrolytic solution was put in a three-pole potential window of electrochemical stability determination cell using a glassy carbon electrode for the work electrode and the counter electrode and an Ag/Ag⁺ electrode as the reference electrode, and the electric potential was scanned at 10 mV/sec by use of a potentiogalvanostat. With the Ag/Ag⁺ electrode used as the reference, the range in which not less than 1 μA of oxidation/reduction decomposition current did not flow was regarded as potential window of electrochemical stability.

Charging/discharging Test:

25 [0062] A charging/discharging test was conducted in which the process of charging a capacitor up to a final charging voltage of 3.5V at a charging current of 3A in an environment at 70°C and then discharging the capacitor to a final discharging voltage of 1.5V at a discharging current of 3A was determined to be one cycle. Under these conditions, the amount of change in the capacity of the wound-type electric double layer capacitor after 10,000 cycles was determined.

30 Example 1:

[0063] 25 milliliters of non-aqueous electrolytic solution were prepared by dissolving 2.17 g (0.01 mol) of tetrafluoroborate tetraethylammonium ((C₂H₅)₄NBF₄) in 4-methacryloyloxymethyl-1,3-dioxolane-2-one (electrolyte concentration: 0.5 mol/liter). The potential window of electrochemical stability of the electrolytic solution thus obtained was determined.

[0064] Moreover, a wound-type electric double layer capacitor with a rated capacity of 2.3V30F (18 mm in diameter 40 mm in length) as shown in Fig.1 and Fig.2 was prepared by using the non-aqueous electrolytic solution obtained as described above as the electrolytic solution, an aluminum foil, that its surface is roughened, coated with a slurry in water of a mixed powder of coconut shell activated carbon powder, acetylene black and carboxymethylcellulose in the prescribed thickness and dried as the polarizable electrode, and nonwoven fabrics made from polypropylene as the separator. A charging/discharging test was conducted on the wound-type electric double layer capacitor.

[0065] Further, in the following Examples, wound-type electric double layer capacitors similar to the one of Example 1 were prepared, and a charging/discharging test was conducted on the wound-type electric double layer capacitors.

45 Example 2:

[0066] 25 milliliters of non-aqueous electrolytic solution were prepared by dissolving 2.71 g (0.0125 mol) of tetrafluoroborate tetraethylammonium ((C₂H₅)₄NBF₄) in 4-acryloyloxymethyl-1,3-dioxolane-2-one (electrolyte concentration: 0.5 mol/liter). The electrolytic solution thus obtained was evaluated in the same manner as described in Example 1. Moreover, a wound-type electric double layer capacitor was prepared in the same manner as described in Example 1 except that the electrolytic solution thus obtained was used. A charging/discharging test was conducted on the wound-type electric double layer capacitor under the same conditions used in Example 1.

[0067] The results are shown in Table 1.

55 Comparative Example 1:

[0068] An electrolytic solution was prepared in the same manner as described in Example 1 except that propylene

[0077] The results are shown in Table 2.

Example 6:

[0078] A non-aqueous electrolytic solution was prepared in the same manner as described in Example 5 except that 4-(1-propenyl oxymethyl)-1,3-dioxolane-2-one was used in place of 4-allyloxymethyl-1,3-dioxolane-2-one. The potential window of electrochemical stability of the electrolytic solution thus obtained was determined. A charging/discharging test was conducted on the wound-type electric double layer capacitor thus obtained in the same manner as described in Example 1.

[0079] The results are shown in Table 2.

Example 7:

[0080] A non-aqueous electrolytic solution was prepared by dissolving 2.71 g (0.0125 mol) of tetrafluoroborate tetraethylammonium ($(C_2H_5)_4NBF_4$) in 4-vinylethylene carbonate (electrolyte concentration: 0.5 mol/liter). The potential window of electrochemical stability of the electrolytic solution thus obtained was determined. A charging/discharging test was conducted on the wound-type electric double layer capacitor thus obtained in the same manner as described in Example 1.

[0081] The results are shown in Table 2.

Example 8:

[0082] A non-aqueous electrolytic solution was prepared in the same manner as described in Example 7 except that 4,5-divinylethylene carbonate was used in place of 4-vinylethylene carbonate. The potential window of electrochemical stability of the electrolytic solution thus obtained was determined. A charging/discharging test was conducted on the wound-type electric double layer capacitor thus obtained in the same manner as described in Example 1.

[0083] The results are shown in Table 2.

Example 9:

[0084] 25 milliliters of non-aqueous electrolytic solution were prepared by dissolving 2.71 g (0.0125 mol) of tetrafluoroborate tetraethylammonium ($(C_2H_5)_4NBF_4$) in a mixed solvent of 4-vinylethylene carbonate and propylene carbonate mixed in a ratio by weight of 5:95 (electrolyte concentration: 0.5 mol/liter). The potential window of electrochemical stability of the electrolytic solution thus obtained was determined in the same manner as described in Example 1. A charging/discharging test was conducted on the wound-type electric double layer capacitor thus obtained in the same manner as described in Example 1.

[0085] The results are shown in Table 2.

Example 10:

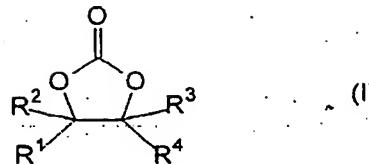
[0086] 25 milliliters of a non-aqueous electrolytic solution was prepared by dissolving 2.71 g (0.0125 mol) of tetrafluoroborate-4-ethylammonium ($(C_2H_5)_4NBF_4$) in vinylene carbonate (electrolyte concentration: 0.5 mol/liter). The potential window of electrochemical stability of the electrolytic solution thus obtained was determined. A charging/discharging test was conducted on the wound-type electric double layer capacitor thus obtained in the same manner as described in Example 1.

[0087] The results are shown in Table 2.

Example 11:

[0088] 25 milliliters of non-aqueous electrolytic solution were prepared by dissolving 2.71 g (0.0125 mol) of tetrafluoroborate tetraethylammonium ($(C_2H_5)_4NBF_4$) in a mixed solvent of propylene carbonate and vinylene carbonate mixed in a ratio by weight of 95:5 (electrolyte concentration: 0.5 mol/liter). The potential window of electrochemical stability of the electrolytic solution thus obtained was determined. A charging/discharging test was conducted on the wound-type electric double layer capacitor thus obtained in the same manner as described in Example 1.

[0089] The results are shown in Table 2.



10

wherein

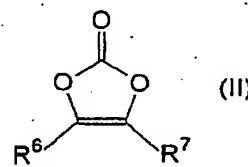
R¹ to R⁴, which may be the same or different, are each hydrogen, optionally substituted alkyl, an optionally substituted unsaturated hydrocarbon group, optionally substituted aryl or a group represented by -CH₂-O-A in which A is R⁵, CO-R⁵ or CO-O-R⁵ and R⁵ is alkyl or an unsaturated hydrocarbon group; said compound being such that:

15

- (i) at least one of R¹ to R⁴ is -CH₂-O-A, with the remaining groups selected from hydrogen, optionally substituted alkyl and an optionally substituted unsaturated hydrocarbon group; or
- (ii) at least one of R¹ to R⁴ is an optionally substituted unsaturated hydrocarbon group, with the remaining groups selected from hydrogen, optionally substituted alkyl, optionally substituted aryl and an optionally substituted unsaturated hydrocarbon group; or
- (iii) R¹ to R⁴ are selected from optionally substituted alkyl and optionally substituted aryl;

(2) is a compound of Formula (II):

25



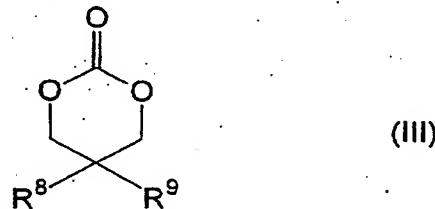
30

wherein

R⁶ and R⁷, which may be the same or different, are each hydrogen, optionally substituted alkyl or an optionally substituted unsaturated hydrocarbon group; and

(3) is a compound of Formula (III):

40



45

wherein

R⁸ to R⁹, which may be the same or different, are each optionally substituted alkyl, optionally substituted aryl or an optionally substituted unsaturated hydrocarbon group.

55

2. A solution according to claim 1, comprising an ester of Formula (I) wherein R¹, R², R³ and R⁴, which may be the same or different, are hydrogen, an alkyl group having 1 to 4 carbon atoms, an unsaturated hydrocarbon group having 2 to 4 carbon atoms or an aryl group having 6 to 12 carbon atoms and at least one of R¹ to R⁴ is an unsaturated hydrocarbon group having 2 to 4 carbon atoms.

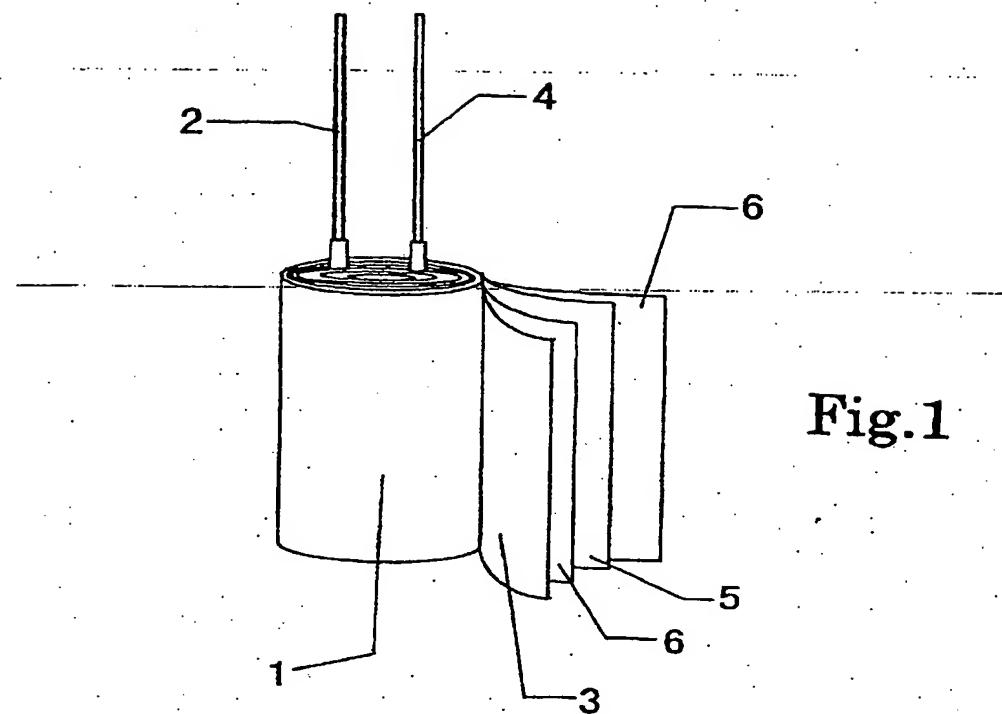


Fig.1

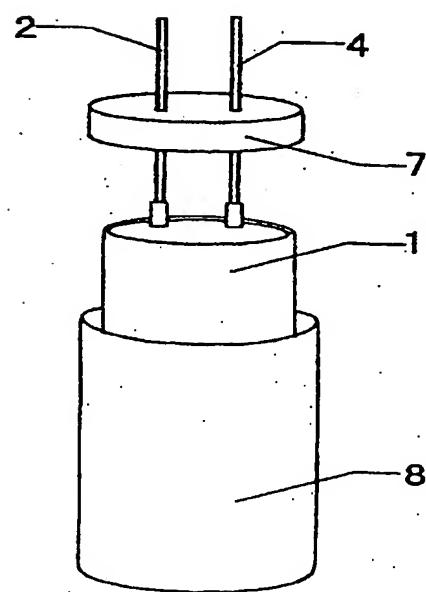


Fig.2